THE

SCIENTIFIC PROCEEDINGS

OF THE

ROYAL DUBLIN SOCIETY

VOL. 25 (N.S.).

No 11. MAY 25, 1950

FRIEDEL-CRAFTS POLYMERISATION

A DISCUSSION

Edited By

D. C. PEPPER

DUBLIN:
PUBLISHED BY THE ROYAL DUBLIN SOCIETY,
BALLSBRIDGE, DUBLIN.
1950

Price: Ten Shillings.

No. 11.

FRIEDEL-CRAFTS POLYMERISATION
A DISCUSSION

EDITED BY

D. C. PEPPER, Trinity College, Dublin.

(*Read January* 24, *Published May* 25)

An informal meeting was held in the Chemical Laboratory, Trinity College, Dublin, on July 5th—7th, 1949, to discuss recent research on the polymerisation of olefines by Friedel-Crafts catalysts. The chairman was Prof. M. G. Evans, F.R.S., of Manchester University, and the following took part in the discussion : Mr. C. M. van Battum (Royal Dutch Shell, Amsterdam), Prof. W. Cocker (Dublin U.), Dr. F. S. Dainton (Cambridge U.), Dr. M. H. Dilke (Bristol U.), Prof. T. Dillon (Univ. Coll., Galway), Dr. D. D. Eley (Bristol U.), Dr. A. G. Evans (Manchester U.), Mr. S. D. Hamann (Manchester U.), Mr. van Keekum (Royal Dutch Shell, The Hague.), Dr. G. W. Meadows (Manchester U.), Dr. L. B. Morgan (I.C.I. Dyestuffs Div.), Dr. D. C. Pepper (Dublin U.), Dr. F. T. Perkins (Manchester U.), Dr. P. H. Plesch (Manchester U.), Dr. A. W. Richards (Bristol U.), Dr. R. F. Tuckett (I.C.I., Plastics Div.), Dr. M. A. Weinberger (Univ. Coll., Hull), Dr. R. B. Whyte (Shell Petroleum Co.).

Of the twelve papers discussed at the meeting six had been submitted to English or American scientific journals (though at the time of the discussion only four had appeared). Such papers are reported here only in summary. The other papers and the discussion are described in greater detail. As shown below, the papers were read in groups according to the subject matter, each group being followed by a general discussion. The main conclusions of the discussion are summarised at the end in a short review by the editor.

CONTENTS.

I.—GENERAL KINETICS.

The Polymerisation of Vinyl Octyl Ether. By D. D. Eley and A. W. Richards.
The Polymerisation of Styrene by Stannic Chloride. By D. C. Pepper.
The Low Temperature Polymerisation of Isobutene. By P. H. Plesch.
General Discussion.—Dr. F. S. Dainton, Dr. R. F. Tuckett, Dr. A. G. Evans, Dr. D. D. Eley, Dr. D. C. Pepper.

2.—Cocatalysts and Initiation Processes.

The Polymerisation of Isobutene catalysed by Boron Trifluoride Complexes. By A. G. Evans and G. W. Meadows.

Spectroscopic Evidence for the presence of Carbonium Ions in Mixtures of Olefines and Friedel-Crafts Catalysts. By A. G. Evans and S. D. Hamann.

Solvent Effects in Friedel-Crafts Polymerisation. By D. C. Pepper.

Suggestions concerning the Ionic Polymerisation of Vinyl Ethers. By S. D. Hamann, P. H. Plesch, and H. A. Skinner.

General Discussion.—Dr. A. G. Evans, Dr. G. W. Meadows, Dr. P. H. Plesch, Dr. F. S. Dainton, Dr. D. D. Eley, Dr. D. C. Pepper, Prof. M. G. Evans, Mr. S. D. Hamann, Dr. L. B. Morgan.

3.—End-Groups and the Termination Process.

The Use of Infra-Red Absorption Spectra to Elucidate Reaction Mechanisms in Ionic Polymerisation. By F. S. Dainton and G. B. B. M. Sutherland.

Infra-Red Evidence of End-Groups in Polyisobutene. By M. St. C. Flett and P. H. Plesch.

4.—Friedel-Crafts Complexes.

Kinetic Examination of the Reactions of Di-isobutene catalysed by Boron Trifluoride Complexes. By A. G. Evans and F. T. Perkins.

Friedel-Crafts Complexes and the Initiation of Polymerisation. By D. D. Eley and M. H. Dilke.

General Discussion.—Dr. A. G. Evans, Dr. D. D. Eley, Prof. M. G. Evans, Mr. S. D. Hamann, Dr. F. T. Perkins, Dr. P. H. Plesch.

5.—The Effect of Temperature.

Some Observations on the Effects of Temperature on Ionic Polymerisations. By F. S. Dainton.

General Discussion.—Dr. P. H. Plesch, Dr. G. W. Meadows, Dr. D. D. Eley, Dr. R. F. Tuckett.

6.—Summary of the Discussion.

By D. C. Pepper.

1.—*GENERAL KINETICS.*

THE POLYMERISATION OF VINYL OCTYL ETHER

BY

D. D. ELEY AND A. W. RICHARDS[1] *Bristol University.*

THE polymerisation of vinyl octyl ether by four catalysts follows the kinetic scheme[2]

$$C + M \longrightarrow M^* \qquad (1)$$

$$M^* + M \longrightarrow M_2^* \text{ etc.} \qquad (2)$$

$$M_n^* \longrightarrow M_n \qquad (3)$$

$$M_n^* + M \longrightarrow M_n + M^* \qquad (4)$$

with the following qualifications. Iodine molecules undergo a preliminary bimolecular ionisation step to give I^+. Silver perchlorate, while showing some activity when anhydrous, is activated by water and in this case probably initiates *via* H^+. Triphenyl methyl chloride acts through the carbonium ion. Stannic chloride is active in the " nearly anhydrous " state. The first three catalysts give products of M.W. $\sim$ 1,000, and the transfer reaction (4) is dominant in chain ending, as is also shown by the independence of molecular weight on initial monomer concentration. For stannic chloride the molecular weight of the product depends directly on initial monomer concentration and may reach 20,000, showing that the spontaneous termination mechanism (3) is operative.

THE POLYMERISATION OF STYRENE BY STANNIC CHLORIDE

BY

D. C. PEPPER.[3]
Dublin University.

IN solutions of styrene in ethylene dichloride at 25°C. the rate of polymerisation is found proportional to the concentration of stannic chloride, and to the square of the concentration of styrene. The molecular weight of the polymer produced is proportional to the styrene concentration, and independent of that of the catalyst.

Traces of water increase the electrical conductivity of these solutions, but decrease the rate of polymerisation. It is concluded that in this system stannic chloride does not need water as a cocatalyst. The conductivities observed are due

[1] Full details in : D. D. Eley and A. W. Richards, Trans. Farad. Soc. **45**. 425 (1949).

[2] The symbols in the scheme have the following significance : C, catalyst ; M, monomer ; M_n, polymer of n monomer units ; M*, activated monomer or polymer.

[3] Full details in Pepper, Trans. Farad. Soc. **45**. 404. (1949).

to ions produced by hydration or hydrolysis of the stannic chloride by adventitious moisture, and not to ions involved in the polymerisation reactions. Similar behaviour is observed in other solvents of high dielectric constant. The initiation process involves one stannic chloride and one monomer molecule. It may, therefore, be the donation of the double bond electrons to the stannic chloride, forming a polarised molecule, or perhaps more likely, the combination of monomer with a carbonium ion produced by interaction of the stannic chloride with the solvent. The termination step is a first order process and is presumably the spontaneous expulsion of the catalyst or carbonium ion. This would mean that the catalyst is regenerated at the end of each polymerisation chain, and would account for the observed formation of many polymer molecules for each catalyst molecule present. Transfer processes do not seem to be important in this system, and are not included in the kinetic scheme.

The Low-Temperature Polymerisation of Isobutene

By

P. H. Plesch,

Manchester University.

The polymerisation of isobutene in hexane solution by $TiCl_4$ with water and trichloracetic acid as cocatalysts was investigated at temperatures between $-90°$ and $0°C.$, using an adiabatic technique, the reaction being followed by the temperature rise. The kinetic data which are of a preliminary nature, show that the reaction is of first order with respect to cocatalyst, and of an order between 1 and 2 with respect to monomer. The M.Wt. of the end-product of reaction shows no significant variation with cocatalyst concentration and only slight dependence on monomer concentration. Provided the catalyst $TiCl_4$ concentration is above a certain value, the rate is independent of it.

Both rate and M.Wt. increase with decreasing temperature and the activation energies E_R and E_M derived from the plots of log (Rate) against $1/T$ and log M against $1/T$ are identical within the limits of experimental error and $= -8 \pm 2$ k.cal/mole. Since the rate and molecular weight are proportional to $k_i k_p / k_t$ and k_p / k_t respectively, then $E_R = E_i + E_p - E_t$ and $E_M = E_p - E_t$ where k_i, k_p, k_t are the rate constants and E_i, E_p, E_t the activation energies for the initiation, propagation, and termination reactions. Therefore, since $E_R \simeq E_M \simeq -8 \pm 2$ k.cal/mole, this means that E_i, the activation energy of initiation, is not greater than 4 kcal/mole and probably much smaller. If, as is probable, E_p is of the same order of magnitude as E_i, E_t must be 6—10 k.cal/mole. This high value is associated with the rearrangement of the ion-pair at the growing end of the polymer chain during termination. Chlorine analysis of low M.Wt. polymers indicates that the cocatalyst may be built into the end of the chain at termination. The polarised-molecule theory advocated by various American authors is shown to be inapplicable to this system, and the carbonium ion theory is developed with an unimolecular chain termination. It is

also shown that bimolecular termination by monomer leading to terminal double bonds in the polymer, and the formation of isobutyl trichloracetate, may be important.

With water vapour as cocatalyst the time-temperature curves are always S-shaped. Using trichloracetic acid as cocatalyst the rate decreases monotonically from the start unless either the ratio catalyst : cocatalyst is less than about 4 or the cocatalyst is added very slowly to the system. The S-curves are explained in all three cases by the slow formation of the initiating complex between catalyst and cocatalyst, leading to a relatively slow build up of the concentration of growing chains.

Discussion.

F. S. Dainton: I can confirm that in solvents of high dielectric constant, moisture is not required as a cocatalyst when silver salts are used. Dr. Eley has mentioned $AgClO_4$ as a catalyst ; Dr. Ivin and I have found $AgNO_3$ and Ag_2SO_4 also to be effective catalysts for polymerisations carried out in liquid sulphur dioxide. During reaction little, if any, silver nitrate is destroyed, and many more polymer molecules are formed than catalyst molecules are present. These facts substantiate the idea that the Ag^+ ion is the real catalytic agent, and is so by virtue of its strong electron pair accepting capacity, *i.e.* its strength as an acid in the G.N. Lewis sense.

Drs. Eley and Richards have proposed a reaction scheme for the iodine-catalysed polymerisation of vinyl octyl ether in which an iodine atom is incorporated in the polymer during initiation, and a proton expelled from the carbonium ion during termination. Have the authors been able to detect the hydrogen iodide which should, therefore, accumulate in the system, or to observe the implicit decrease in the free iodine concentration ?

The papers presented in this (general kinetic) section illustrate vividly the need for molecular weight determinations of the highest accuracy in studying ionic polymerisations. Without such data we cannot be sure (*a*) whether monomer transfer is occurring and, if so, is in some way a function of the catalyst used, and (*b*) of the sign and magnitude of $E_p - E_t$. These are two questions wherein we may find the answers to be different from radical polymerisations. The specific action of the catalyst referred to in (*a*) above is not altogether unexpected if the gegen anion is always in loose association with the growing end of the polymer.

Dr. Plesch has mentioned that the activation energy for propagation may be zero in the low temperature polymerisation of isobutene. As I hope to show later, this difference from radical polymerisation may be attributed to the ion-induced dipole forces.

R. F. Tuckett: I would like to add a note of caution about the interpretation of kinetic measurements. Any deduction about mechanisms which depends on the variation of rate and/or molecular weight with monomer concentration should at least be made with care. This is recognised in photochemical radical polymerisa-

tion where nothing can be deduced from the observed "order" of the reaction without extra information about the absorption of light by the monomer. Similarly, in catalysed polymerisations, the initiation process can be written either as a single stage process

$$M + C \longrightarrow P_1$$

or as one which involves two successive reactions

$$C \longrightarrow R \quad \text{(slow)}$$

$$R + M \longrightarrow P_1 \quad \text{(faster)}$$

For mutual termination, the first process gives Rate $\propto M^{3/2}$ while the second alters this to Rate $\propto M$. Similar complications may exist in ionic polymerization, and any deductions about mechanisms from the observed order of the reaction should be backed up by independent evidence.

In the remarks on transfer, there is a tendency to infer that because molecular weight is independent of monomer concentration, transfer is present. This fits in with other evidence, but is not sufficient by itself. Independence of catalyst concentration is a much surer criterion, though in the ionic case spontaneous termination (by proton expulsion) ensures that catalyst concentration does not appear in the molecular weight expression. In radical polymerisations it is perfectly possible to have the molecular weight depending on the monomer concentration in a system with a great deal of transfer going on; this is because solvent transfer plays a part here in depressing the molecular weight.

If one examines the two schemes put forward by Eley and Richards and by Pepper, they do differ slightly; both have to explain the fact that one molecule of catalyst starts off many more than one polymer chain. Pepper suggests

$$P_n \longrightarrow M_n + C \qquad (1)$$

which regenerates the catalyst, while Eley and Richards introduce a monomer transfer mechanism

$$P_n + M \longrightarrow M_n + P_1 \qquad (2)$$

(P_n is active polymer and M_n is dead material) in addition to the normal process of spontaneous termination.

$$P_n \longrightarrow M_n \qquad (3)$$

It is not clear whether the two termination processes are identical, but, in any case, equation (1) combined with normal slow initiation step does, in effect, give equation (2) — is it not possible that, in spite of the observed kinetics, the monomer termination process does not exist and that equation (1) represents a sufficient mechanism?

A. G. Evans: I should like to ask Dr. Eley for a more detailed picture of his mechanism for the stannic chloride polymerisation. In that mechanism he writes the unimolecular spontaneous termination of the chain as a regeneration of the catalyst molecule (Trans. Farad. Soc., **45**, 443, 1949). But in his explanation of the higher molecular weights obtained for $SnCl_4$ as catalyst he suggests that the $SnCl_4$ may be assumed to start two chains. Here, presumably, the $SnCl_4$ is assumed to act as a link between the two chains and cannot be regenerated by a spontaneous unimolecular reaction.

D. D. Eley: If we consider the data of Eley and Richards on the stannic chloride catalysed polymerisation of vinyl octyl ether, we find the following at 25°C.

$$\frac{k_i . k_p}{k_t} = 2.4 \times 10^7 \text{ litres}^2 \text{ mol.}^{-2} \text{ min.}^{-1}$$

$$\text{Degree of Polymerisation} = \bar{\mathbf{P}} = 70.5 = \frac{k_p}{k_t} . [M]$$

$$\text{i.e. } \frac{k_p}{k_t} = 117 \text{ litre mol.}^{-1}$$

$$\text{Hence } k_i = 0.34 \times 10^4 \text{ litre mol.}^{-1} \text{ sec.}^{-1}$$

If we take the activation energy for initiation as $E = 13{,}300$, then A in $k_i = A.e^{-E/RT}$ is 1.6×10^{13} litres mol.$^{-1}$ sec.$^{-1}$. Dr. Dainton has drawn attention to the fact (noted in the paper) that the log $k - 1/T$ plot is not a straight line. If we allow an inaccuracy of ± 2000 cal. then the inaccuracy in the A factor is a factor of 30 fold greater or less. Let us say that in round figures the A factor lies between 10^{11} and 10^{13}, *i.e.* it corresponds to a somewhat faster rate than the normal bimolecular reaction (normal value 2×10^{11}). I do not wish to press the application of this data of low accuracy, but merely to point out that there is no marked anomaly in the A factor such as that found in the uncatalysed polymerisation of styrene where A is 10^1 litre mol.$^{-1}$ sec.$^{-1}$. Eyring has shown us how such low A factors are associated with an excited triplet state of the double bond. Since the lowest *ionic* state of the double bond, with which we are concerned here, has presumably a *singlet* state, Eyring's theory indicates that a more or less normal A factor is to be expected.

Transfer to monomer :—In the same system (vinyl octyl ether, stannic chloride) Eley and Richards have drawn attention to the abrupt increase at about 50°C. in the falling off of the molecular weight with temperature. The calculated " activation energies " are

E_M (25—50°C.) —3.3 k.cal.

E_M (55—60°C.) —40 k.cal.

I have recently plotted the data on isobutene (Thomas *et al.* J.A.C.S., **62**. 276) and α-methyl styrene (Hersberger *et al.* Ind. Eng. Chem., **37**.1073) but over the whole of the temperature ranges concerned $E_M \approx -3$ k.cal. Although there is some effect of temperature on E_M, the effect is small, and there is no abrupt change in slope. The highest temperatures concerned were, however, below room temperature, and so it is possible that a sudden change of slope may set in at higher temperature.

On Dr. Plesch's paper :—The significance of the molecular weight data reported will depend on whether the reaction was always stopped at the same percentage polymerisation, particularly if there is any increase in the average molecular weight with time, as may occur when the concentration of active centres is changing.

To Dr. Dainton's query :—We did not attempt to estimate whether HI was produced in the iodine catalysed polymerisation.

On Dr. A. G. Evans' point :—We have not formulated any firm views on the molecular nature of the catalystpolymer complex. The view we held tentatively

was that termination of $SnCl_4$—initiated polymers involved expulsion of HCl, *i.e.* if two chains were started the product would be :

$$CHR{=}CH_2{-}(CHR{-}CH_2)_n{-}\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\underset{|}{\overset{|}{Sn}}}}{-}(CH_2{-}CHR)_m CH_2{=}CHR + 2HCl$$

D. C. Pepper: It can be shown that in the stannic chloride catalysed polymerisation of styrene, no appreciable amount of the polymer formed has the structure suggested by Dr. Eley, *i.e.* with a central $-SnCl_2-$ group. Such a group would be removed by hydrolysis, and the polymer chain broken, on the average, into two equal fragments. The intrinsic viscosity of the polymer measured without isolation should, therefore, be approximately twice that of polymer isolated after hydrolysis. In an experimental test of this point, the intrinsic viscosity of the polymer was found to be unaffected by hydrolysis.

2.—*COCATALYSTS AND INITIATION PROCESSES.*

The Polymerisation of Isobutene Catalysed by Boron-trifluoride Complexes

By

Alwyn G. Evans and G. W. Meadows,
Manchester University.

The polymerisation of isobutene by boron-trifluoride requires a cocatalyst both for the room temperature low molecular weight reaction, and for the rapid low temperature high molecular weight reaction. The boron-trifluoride forms a complex with the cocatalyst. Excess boron-trifluoride is required to stabilise the active 1:1 boron-trifluoride : cocatalyst complex.

The reaction does not occur in the gas phase. The slow reactions at room temperature show a very good first order dependence on isobutene pressure. There is thus no falling off of catalyst activity during these slow reactions. The first order constants for the slow reactions are proportional to the first power of the total cocatalyst present (boron-trifluoride in excess). In the room temperature low molecular weight reaction, one cocatalyst molecule caused more than 2,000 polymer molecules to be formed.

Initiation consists in a proton transfer from the catalyst complex to the olefin molecule. Under the conditions of these experiments the positive end of the growing chain must always be in contact with the negative catalyst residue. Chain termination consists in proton transfer from the carbonium ion either to the negative catalyst residue to reform the catalyst, or to another monomer molecule. The fact that at room temperature, the molecular weight of the product increases with increase in monomer pressure shows that proton transfer from the carbonium ion to

the negative catalyst residue is an important termination mechanism in these reactions.

The stopping of the polymerisation of isobutene by boron-trifluoride at low temperature requires extreme precautions in the removal of impurities from the reaction system. This was achieved (*a*) by introducing the purified boron-trifluoride into a vessel containing a freshly distilled film of sodium, and (*b*) by introducing the purified isobutene into a vessel shaped like an annular ring which also contained freshly distilled sodium. Both vessels were sealed off and did not contain any taps. Junction between the two vessels, and hence the mixing of the two gases could be brought about by breaking a glass seal by means of a magnetic breaker. The isobutene was first circulated over the heated sodium (100°C.) for 12 hours (circulation being achieved by convection), and then the system was allowed to cool, and the two gases mixed. This gas mixture was condensed and re-evaporated several times in different parts of the vessel without polymerisation occurring. On introducing moist air, however, the condensed system polymerised instantaneously to give a solid polymer.

Spectroscopic Evidence for the Presence of Carbonium Ions in Mixtures of Olefins and Friedel-Crafts Catalysts

By

Alwyn G. Evans and S. D. Hamann,
Manchester University.

We have treated $\alpha\alpha$-diphenyl ethylene ($Ph_2C{=}CH_2$) with Friedel-Crafts catalysts to see if carbonium ions are formed by proton addition to the double bond. The presence of the phenyl groups means that any carbonium ions so formed will be stabilised and made more easily identifiable spectroscopically. The presence of these α-phenyl substitutents also stops the polymerisation at the dimer, probably on account of steric hindrance.

The ultra-violet absorption spectrum of the carbonium ion Ph_3C^+ gives a marked absorption peak at 431 mμ (Ph_3CHSO_4 in conc. H_2SO_4, Hantzsch, Ber., **54**, 2573, (1921); Anderson, J.A.C.S., **52**, 4567, (1930)). The solution of $Ph_2C{=}CH_2$ in conc. H_2SO_4 shows a very similar spectrum with a peak at 434 mμ. This spectrum is quite different from that of $Ph_2C{=}CH_2$ itself, and we attribute it to the presence of the carbonium ion $Ph_2\overset{+}{C}{-}CH_3$.

This absorption peak was also obtained when $Ph_2C{=}CH_2$ was brought into contact (*a*) with a solution of boron-trifluoride in benzene (which had not been subjected to any rigorous drying, and which, therefore, contained the acid F_3BOH_2) 430 mμ, and (*b*) with a suspension of activated floridin (which is known to act as an acid) in paraffin, 430—440 mμ.

When $SnCl_4$ is added to $Ph_2C{=}CH_2$ a weak absorption in the same region is obtained. When HCl is bubbled through this solution the absorption increases greatly in intensity. We thus believe that the weak absorption in the $SnCl_4$,

$Ph_2C{=}CH_2$ mixture is due to the presence of some HCl impurity, and that a mixture of the pure components would show no interaction.

Schoepfle and Ryan have found an absorption peak at 435 mμ for $Ph_2.C.(Cl).CH_3$ plus $SnCl_4$ in ethylene dichloride. (J.A.C.S., **54**, 3689, (1932)). This agrees closely with the absorption peak of 434 mμ which we find for a solution of $Ph_2C{=}CH_2$ in H_2SO_4, and we attribute it to the ion $Ph_2.\overset{+}{C}.CH_3$. We have found that a solution of $Ph_2.C.(Cl),CH_3$ in ethylene dichloride plus $SnCl_4$ shows an electrical conductivity, which suggests that appreciable dissociation occurs giving the cation $Ph_2.\overset{+}{C}.CH_3$ and possibly the anion $\bar{S}nCl_5$.

The fact that the spectrum is the same for all our cases, even though the acids are different, is strong indication that in our experiments the olefin double bond takes up a proton to form a carbonium ion, and is not merely polarised, since the spectrum of a polarised olefin would be expected to differ markedly with change in the nature of the polarising group.

The spectrum of $Ph.C(CH_3){=}CH_2$ in conc. H_2SO_4 also indicated the presence of ions.

The stability of the $Ph_2.\overset{+}{C}.CH_3$ and $Ph.\overset{+}{C}(CH_3)_2$ ions is very much less than that of the Ph_3C^+ ions, as is to be expected. The effect of alcohols and water in discharging the colour of these ions in sulphuric acid solution is much greater than in the case of the Ph_3C^+ ions.

Solvent Effects in Friedel-Crafts Polymerisation

By

D. C. Pepper.[1]

It has been shown that for several olefines (styrene, *a*-methyl styrene, vinyl butyl ether) polymerised in solution at ordinary temperatures by stannic chloride and other Friedel-Crafts catalysts both the rate and degree of polymerisation are increased by increasing the dielectric constant of the solvent. This effect is taken as qualitative evidence for the presence of ionic processes in these polymerisations. The dependence of rate of polymerisation on dielectric constant of the solvent is very marked (approximately 100 times greater in nitrobenzene than in hydrocarbons), and over a range of solvents is approximately exponential, though the exact form of this dependence is not yet established with certainty. The effect on the chain length is slighter, showing only a five-fold increase from hydrocarbons to nitrobenzene.

An increase of dielectric constant should increase the rate of initiation (formation of ions), and reduce the termination rate (destruction of ions). The greater influence on rate than on molecular weight implies that the former is the dominant effect. This may be due to the acceleration of an ionisation reaction or, more probably, to a shift in an ionisation equilibrium towards a higher concentration of initiating ions.

[1] Full details in Pepper, Trans. Far. Soc. **45** 397. (1949).

Ions produced by hydrolysis or hydration of stannic chloride by traces of water can be detected by conductivity measurements in solvents of high dielectric constant ($\varepsilon > 10$), but are shown to be not responsible for the polymerisation in these solvents. Water as a cocatalyst may be necessary in hydrocarbon solvents.

The conclusion that added cocatalysts are not necessary in solvents of high dielectric constant raises the question whether the halide itself can be the effective initiator, or whether it must form a complex with the solvent, which then dissociates to give the initiating ions. If the latter is the case, then we should expect specific effects of solvent according to the ease of complex formation, as well as the general effect of dielectric constant. The nitroparaffins might be expected to show such specific effects, since it is found that solutions of stannic chloride in these solvents show very high conductivity, *i.e.* ionisable complexes are easily formed. Preliminary experiments have indicated that the rates of polymerisation in these solvents are about what would be expected from their dielectric constants, but that the degree of polymerisation is anomalously low.

Suggestions Concerning the Ionic Polymerisation of Vinyl Ethers.
(as amended November, 1949)

By

S. D. Hamann, P. H. Plesch and H. A. Skinner,
Manchester University.

Eley and Pepper (1) and Eley and Richards (2) have recently studied the kinetics of the catalysed polymerisation of vinyl ethers. The very simple formal scheme which accounts adequately for the kinetics of these reactions does not provide a definite picture of the mechanism of the reaction. Nor does the oxonium theory of Shostakovskii (3) appear adequate to explain the observations. Our suggested explanation of the observed facts arises from the following considerations.

It is difficult to see how the presence of two double bonds in each polymer molecule (reported by Eley and Richards for the polymerisation of 2-ethyl hexyl vinyl ether) can be explained without assuming that the chain is started by an unsaturated entity, and that the second double bond is formed in the termination process. Since the chain growth is almost certainly a carbonium ion process the initiating entity must be a positive ion of some sort. We assume therefore that the ether is split into two ions under the influence of the catalyst. This may obviously occur in two different ways, but energetic considerations can show which of these will in fact take place.

Process I $\quad R{-}OCH{=}CH_2 \longrightarrow R^+ + CH_2{=}CHO^-$

This requires an amount of energy given by

$$E_1 = D(R{-}OCH{=}CH_2) + I(R) - A(OCH{=}CH_2)$$

Process II $\quad RO{-}CH{=}CH_2 \longrightarrow RO^- + CH_2{=}CH^+$

requires $\quad E_2 = D(RO{-}CH{=}CH_2) + I(CH{=}CH_2) - A(OR)$

where R represents the 2-ethyl hexyl radical, D is the bond dissociation energy, I the ionisation potential and A the electron affinity of the entity in brackets after the symbol. We now make the plausible assumption that the difference between the two electron affinities concerned is negligible compared with the differences in D and I. Writing V for the vinyl radical, we put

$$\triangle D = D(\text{R—OV}) - D(\text{RO—V})$$

Therefore

$$E_1 - E_2 = I(\text{R}) - I(\text{V}) + \triangle D$$

If this is negative, *i.e.* if more energy is required for Process II than for Process I, the latter will be more likely.

We can estimate $\triangle D$ as follows: The two bond dissociation energies are given by

$$D(\text{R—OV}) = D_1(\text{O—C}) - R(\text{R}) - R(\text{OV})$$
$$D(\text{RO—V}) = D_2(\text{O—C}) - R(\text{OR}) - R(\text{V})$$

where D_1(O—C) and D_2(O—C) are standard or normal bond energies and are assumed to be equal to a first degree of approximation. The R terms are the resonance energies of the radicals indicated in brackets.

Therefore

$$\triangle D = R(\text{OR}) - R(\text{OV}) + R(\text{V}) - R(\text{R}).$$

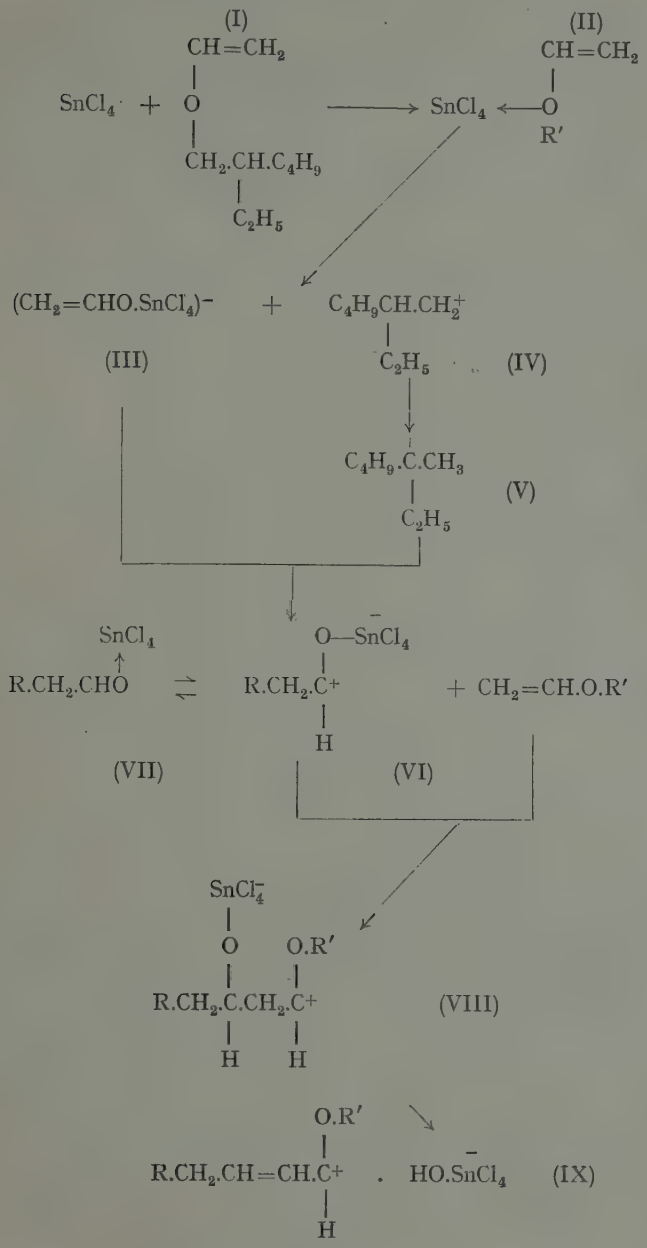
R(V), R(R), and R(OR) are probably small, but R(OV) is likely to be relatively large, since the O—CH=CH_2 radical is similar electronically to the allyl radical. Because of the dissymmetry of the resonance structures A and B

$$\underset{\text{A}}{\text{O=CH—}\dot{\text{C}}\text{H}_2} \qquad \underset{\text{B}}{\dot{\text{O}}\text{—CH=CH}_2}$$

the resonance energy may not be as large as in the allyl radical itself, and we may estimate it at about half of this. If we take the resonance energy of the allyl radical as about 20 k.cal/mole we get for R(OV) about 10 k.cal/mole. R(OR)—R(R) will certainly not be large enough to offset this if it is positive, or to increase it appreciably if it is negative. We thus arrive at an estimate of —10 k.cal/mole for $\triangle D$.

I(V) is known to be 228 k.cal/mole (4). The ionisation potential of the 2-ethyl hexyl radical is not known, but we may estimate that it is unlikely to differ materially from that of the n-propyl radical, which is 180 k.cal/mole (5). Therefore $E_1 - E_2 =$ 180—228—10 *i.e* approximately —60 k.cal/mole. This difference is so large that we consider the results of our argument to be unaffected by any possible differences in the heats of coordination of the alternative oxygen-containing fragments with the catalyst, and by possible differences in the heats of solution of the alternative ions. These considerations therefore indicate strongly that Process I will actually take place. That vinyl allyl ethers do, in fact, split in the manner postulated above is suggested by the occurrence of butyl benzene in the products of reaction of vinyl butyl ether and benzene in presence of $AlCl_3$ (6). No styrene is formed.

The whole reaction by which the initiating ion is formed may be pictured as taking place in the following steps :—

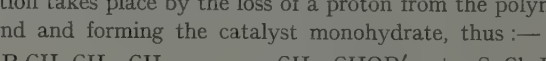


The ether-catalyst complex (II) splits into a complex anion (III) and a carbonium ion (IV), which rearranges to the configuration of maximum stability (V). This

carbonium (V) could itself initiate polymerisation, but it is more likely that it attacks the double bond of the closely associated anion (III), giving the double ion (VI) in equilibrium with the aldehyde (VII). Rearrangements of the type (I)—(VII) have been observed for vinyl ethers (7), and a closely parallel isomerisation is that of isobutyl phenyl ether into para-tertiary butyl phenol under the influence of $AlCl_3$ (8). It is unlikely that the steps from (II) to (VI) take place in a well defined succession. The process probably proceeds by a single intramolecular transformation.

It is considered that the rate determining step in the initiation process is the attack of the positively charged carbon atom of (VI) upon a monomer molecule to give (VIII). This double ion must then, or at an early stage in the polymerisation, *rearrange* to the associated ions (IX), if the charge separation is not to become too great. The configuration of the growing polymer chain is therefore :—

The termination takes place by the loss of a proton from the polymer chain, leaving a double bond and forming the catalyst monohydrate, thus :—



(X)

Aldehydes of the type (VII) are effective reagents in Friedel-Crafts condensations, and it has been reported that in some conditions diolefines are formed from aldehydes and olefines in the presence of BF_3 and water (9). This latter process is analogous to the reaction (VII) ——→ (X). This scheme gives a rate of initiation which is of the first order in monomer if the concentration of (VII) depends only on the $SnCl_4$ concentration (monomer in great excess). It also accounts for the observed unimolecular termination, because in a hydrocarbon solvent the ions cannot be separated, and it explains the presence of two double bonds per polymer molecule. According to the suggested mechanism *the monomer itself acts as cocatalyst*, so that this reaction can now be regarded as a special case of the ionic hydrocarbon polymerisations. The indifference of the initial reaction rate to the presence of water (2) also becomes intelligible in terms of the suggested reaction scheme. Moreover, the slow increase in the reaction rate observed with the n-butyl vinyl ether (but not with the 2-ethyl hexyl ether) which was ascribed to a slow increase in the number of growing polymer chains (1) may find a more detailed explanation in the following terms. The initial formation of the carbonium ions analogous to (V) will probably be much slower for the n-butyl vinyl ether than for the 2-ethyl hexyl vinyl ether, so that the formation of the chain-initiating species will be slow and possibly rate-determining. This condition has been shown by Plesch (10) to account for the S-shaped reaction curves found in other ionic polymerisations.

References.

(1) D. D. Eley and D. C. Pepper, Trans. Farad. Soc., **43**. 112. (1947).
(2) D. D. Eley and A. W. Richards. Trans. Farad. Soc., **45**. 425. (1949).

(3) M. F. Shostakovskii, Doklady Akad. Nauk S.S.S.R. **41**. 120. (1943).
(4) D. P. Stevenson, J.A.C.S., **65**. 209. (1943).
(5) A. G. Evans, Trans. Farad. Soc., **42**. 719. (1946).
(6) V. V. Korshak, K. K. Samplavskaya and A. I. Gershanovich, J. Gen. Chem., **16**. 1065. (1946), C.A., **41**. 2715.
(7) C. D. Hurd, and M. A. Pollak, J. Org. Chem., **3**. 550. (1938).
(8) C. Hartmann and L. Gattermann, Ber., **25**. 3531. (1892).
(9) R. Rosen and E. Arundale, U.S.P. 2368494 (1945), C. A. **39**. 4529.
(10) P. H. Plesch, J.C.S., in the press.

Discussion.

On Drs. Evans' and Meadows' paper.

A. G. Evans: We find that the reaction is first order in isobutene pressure only in the case of the very slow reactions (*e.g.* when BF_3 is mixed with isobutene containing 0.01% of cocatalyst). Under these conditions we find that the polymer liquid is clear. In the faster reactions, when there is more cocatalyst present, the reaction is not first order in isobutene pressure, and the polymer liquid is cloudy, presumably due to the presence of large amounts of the polar BF_3—cocatalyst complex. We have shown that no reaction occurs in the gas phase in any of these reactions. In the fast reactions the cloudiness of the liquid polymer shows that we have a heterogeneous system. We are carrying out experiments to determine whether the very slow reactions which give a good first order in isobutene pressure and a clear polymer liquid are homogeneous reactions occurring in the liquid polymer as solvent, or whether they also are heterogeneous reactions.

We believe that the 1 : 1 boron trifluoride cocatalyst complex, BF_3XOH, is more active than the 1 : 2 complex $BF_3(XOH)_2$. The 1 : 1 complex will be a stronger acid, since the 1 : 2 complex is internally compensated, *e.g.* solid $BF_3.2H_2O$ has the structure

$$(BF_3OH)^-.\cdot(OH_3)^+$$

(Klinkenberg and Ketelaar, Rec. Trav. Chim. **54**, 959, (1935).).

G. W. Meadows: Meerwein (Ber., **66**, 411 (1933)) has shown that the action of BF_3 on ethylene glycol gives a 1 : 1 complex only, (although both 1 : 1 and 1 : 2 complexes are normally found with the monohydroxy alcohols). This result may be explained by the fact that here the 1 : 1 complex itself is internally compensated thus :—

$$\begin{array}{l} CH_2\text{—}\overline{O}\text{—}BF_3 \\ | \\ CH_2\text{—}\overset{+}{O}\text{—}H_2 \end{array}$$

If this is the case, we should not expect this complex to be a very good catalyst for polymerisation.

P. H. Plesch: There can be little doubt about the heterogeneity of the isobutene polymerisation in hexane initiated by titanium tetrachloride and water.

Orange-red crystals are always found in the opaque solutions. The reactions cocatalysed by water vapour are very irreproducible. The variation of initial and maximum rates with temperature both lead to an overall activation energy of ~ 7 to 10 k.cal. per mole. This is interpreted as indicating that the reaction between dissolved $TiCl_4$ and the dispersion of ice particles is the rate-governing step. By comparing this result with the overall activation energy of -8 ± 2 found in the case of cocatalysts by Trichloracetic acid, the energy of activation of the $TiCl_4$—ice reaction can be estimated as 15—20 k.cal per mole.

When $TiCl_4$ is added to a solution of isobutene in hexane at —100 to 120°C. containing very little moisture, polymer is formed very rapidly and predominantly around the glass fittings in the reaction vessel (stirrer, thermometer, etc.) suggesting that the moisture film on the glass is acting as cocatalyst.

F. S. Dainton: There is ample evidence to indicate that the vapour phase polymerisation induced by certain BF_3—cocatalyst complexes is a heterogeneous reaction on the surface of the crystallites. Such crystal surfaces may be highly polar. Thus we know that $BF_3.2H_2O$ has a crystal structure like $HClO_4.H_2O$, and should be written $[H_3O]^+.[BF_3OH]^-$. Heterogeneous polymerisation of a vapour like isobutene may thus be envisaged as follows. First, isobutene is absorbed on the crystal surface, and may at a number of points pick up a proton to form the initiating ion $(CH_3)_3C^+$. Propagation occurs along the surface, linking (and probably desorbing) adjacent monomer molecules. The positive charge is probably never far from an anionic site, so that the 'gegen ion' condition is satisfied. Termination of growth and possible detachment of dead polymer may occur when the carbonium ion growing end finds itself over a 'proton defect' in the surface, *i.e.* a point in the lattice from which a proton has been lost either by a previous initiation process or by other means. At such points the carbonium ion surrenders a proton.

D. D. Eley: It would be interesting to examine whether pure crystalline $BF_3.CH_3COOH$ complex, added from an ampoule broken under the surface of liquid isobutene, could initiate polymerisation.

One possible difficulty in Dr. Dainton's mechanism is that we should expect rather a slow rate of desorption of long chain compounds at low temperatures such as —80°C., so that it is not easy to see how a *rapid* polymerisation could occur.

D. C. Pepper: Desorption of the polymer from the crystal surface is not necessarily a serious difficulty. We should expect the monomer, with its highly polarisable double bond, to be strongly adsorbed on an ionic crystal surface, but the polymer has a saturated, *i.e.* only slightly polarisable, chain, and might be expected to 'peel off' as formed, leaving only the ionic growing end of the chain in association with the surface.

M. G. Evans: The discussion of Drs. Evans and Meadows' paper has emphasised the possibility that the BF_3—cocatalyst-isobutene polymerisation may be heterogeneous. Such heterogeneous polymerizations certainly can occur

in other systems, *e.g.* on fuller's earth and other activated clays. If this is so, the mechanism of the reaction may be different from the homogeneous polymerisation in solution of the vinyl ethers and styrene.

The mechanism postulated by Evans and Meadows' involves spontaneous termination rather than transfer, and the loss of a proton as the actual terminating step. The infra red evidence of Dainton and of Plesch (see later in the discussion) confirms this. If the catalyst complex must, therefore, give up a proton to the monomer in the initiation process, and accept one in the termination step, we might expect a correlation between the strength of a catalyst as an initiator and its weakness as a terminator. Is there any evidence that the more active catalysts give higher molecular weight polymer?

On Drs. Evans' and Hamann's paper

A. G. Evans: We do not believe that the observations we have made indicate that free carbonium ions, as opposed to ion clusters or ion pairs, are present in all the solutions we have studied. For example, in the case of floridin the colour is located on the surface of the clay particles.

S. D. Hamann: In the solutions of Ph_3CCl in m-cresol used as catalyst in the vinyl octyl ether polymerisations described by Dr. Eley, the concentration of free Ph_3C^+ ions is probably extremely small, and this suggests that initiation is brought about by the associated ions.

M. G. Evans: Drs. Evans and Hamann have demonstrated the formation of carbonium ions from a non-polymerising olefin. Is there any spectroscopic evidence for the presence of such ions in polymerising systems, *e.g.* do colours develop during polymerisation?

L. B. Morgan: Blue colours frequently appear in the polymerisation of vinyl butyl ether by BF_3.

G. W. Meadows: Colours develop in BF_3—isobutene only on exposure to air.

D. C. Pepper: In styrene or vinyl butyl ether polymerised by $SnCl_4$, slight yellow colours develop, but only towards the end of the reaction and on standing. These colours are destroyed by water or other hydrolytic solvents, and are, therefore, probably due to ionic complexes of the $SnCl_4$. However, these complexes are more likely to arise from traces of impurities, *i.e.* oxygenated compounds or other substances produced by action of the $SnCl_4$ on the solvent. Thus, solutions of $SnCl_4$ in nitrobenzene or ethylene dichloride slowly develop a crimson colour in the absence of any polymerisable monomer, especially if exposed to air and

traces of moisture. Highly coloured complexes between $SnCl_4$ and ketones are well known.

The evolution of heat remarked by Evans and Hamann when HCl is passed into a solution of $Ph_2C=CH_2$ in $SnCl_4$ suggests that HCl is being added on to the double bond forming $Ph_2.CH_3.C.Cl$. This could then give rise to carbonium ions with the $SnCl_4$ as stated in their paper. Can any appreciable amounts of $Ph_2CH_3C\,Cl$ be isolated from this system?

F. S. Dainton: I should not expect colour to be developed from $Ph_2C=CH_2$ and $SnCl_4$ alone, as the hydrocarbon is not sufficiently electronegative to form a complex with stannic chloride.

It was stated that $Ph_2C=CH_2$ was chosen for these experiments because it does not polymerise. I should expect that it will very possibly do so at low temperatures, and is unaffected at room temperature only because it is above its 'ceiling temperature', due to its low heat of polymerisation which is characteristic of all vinylidene compounds.

A. G. Evans: One must be very careful in attributing colours to carbonium ions, since many colours may be produced which are not due to carbonium ions at all.

P. H. Plesch: The demonstration by Evans and Hamann that activated floridin (attapulgite) can cause the formation of carbonium ions from 1 : 1 diphenyl ethylene is of the utmost importance. The similarity of the products obtained by the action of strong acids and activated clays respectively on olefins has made it appear probable that the nature of the catalysis was the same in the two cases, and Pauling (Nature of the Chemical Bond) has calculated that alumino-silicic acid should be about as strong as perchloric acid. But never before have the phemonena of acid catalysis and clay catalysis been unified so convincingly.

On Dr. Pepper's paper:

F. S. Dainton: An increase of rate (R) with dielectric constant (ε) is to be expected if any of the reaction steps involve charge separation. Suppose the equilibrium constant of the initiating ion production process is K, then the rate of initiation of chains will be proportional to $K^{1/2}$ and hence to $\exp.(-\Delta H^\circ/2\varepsilon RT)$ where ΔH° is the heat of charge separation in vacuo. Hence under conditions of constant temperature and composition $\log R=\alpha-\beta/\varepsilon$, where α and β are constants. Experiments along the lines of those described by Pepper and Eley may yield results which may be explained quantitatively in this way.

M. G. Evans: It should be possible to decide between complete ionic dissociation and ion-pair formation from the form of the relation between rate and dielectric constant. In any case the qualitative effect would be the same; the initiation step would be accelerated, and the termination rate slowed down by an increase in the dielectric constant of the medium. The greater effect on the rate

than on the molecular weight can be explained, since the dielectric constant has a twofold effect on the rate, *i.e.* in increasing k_i and decreasing k_t, whereas it has only a single effect on the molecular weight, in decreasing k_t.

3.—*END-GROUPS AND THE TERMINATION PROCESS.*

THE USE OF INFRA-RED ABSORPTION SPECTRA TO ELUCIDATE REACTIONS MECHANISMS IN IONIC POLYMERISATION.

BY

F. S. DAINTON AND G. B. B. M. SUTHERLAND.[1]
Cambridge University.

BANDS which are present in the infra-red absorption spectra of low molecular weight samples of a polymer, but which are absent from high molecular weight samples of the same substance, are due to the end-groups, and to any catalyst present, if this has not been removed. Applying this principle to the differences between the infra-red spectra of low molecular weight polyisobutenes (D.P. c. 10), obtained by polymerisation of isobutene gas using BF_3 as catalyst and D_2O as cocatalyst, and that of high molecular weight polyisobutene it is shown that :—(*a*) the dominant end-groups are $—C(CH_3)_3$ and $—CH_2.C(CH_3)=CH_2$, (*b*) the cocatalyst is converted progressively from D_2O to H_2O as the reaction proceeds, (*c*) the polymer contains C—D linkages when D_2O is the cocatalyst, (*d*) $(CH_3)_2CH—$ groups are undetectable, but (*e*) traces of $(CH_3)_2C=CH—$ and $—CH_2—C(CH_3)_2OH$ may be present. Conclusions (*a*), (*b*), (*c*) and (*d*), are based on strong bands and well established correlations, and together with the general experience of all workers in this field that the number of polymer molecules formed exceeds the number of catalyst molecules, provide strong evidence in support of the mechanism advanced by Polanyi and others. This may be written in this instance as :—

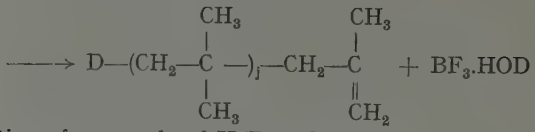
Initiation $BF_3.D_2O + CH_2=C(CH_3)_2 \longrightarrow BF_3OD^- + DCH_2—C^+(CH_3)_2$

N.B. (1) beginning of H/D exchange
(2) t-butyl end-group formed.

Propagation $m_j^+ + m_1 \longrightarrow D—(CH_2—C(CH_3)_2—)_{j+1}^+$

Termination $D—(CH_2—C(CH_3)_2—)_{j+1}^+ + BF_3OD^-$

[1] Full details of this work may be found in J. Polymer Science, **4**. 37. (1949).



N.B. (1) completion of one cycle of H/D exchange
(2) catalyst-cocatalyst complex regenerated
(3) vinylidene end-group formed.

Infra-Red Evidence on End-Groups in Polyisobutene

By

M. St. C. Flett, Imperial Chemical Industries and P. H. Plesch, Manchester University.

The infra-red absorption spectra of polyisobutenes of low molecular weight have been examined and compared with those of high M.Wt. specimens, in order to discover the nature of the *end-groups* (1) (2). Most of the low M.Wt. specimens were prepared in hexane solution by an isothermal technique at 0°C, using $TiCl_4$ as catalyst and CCl_3COOH, $CHCl_2COOH$, H_2O and H_2SO_4 as cocatalysts.

With all cocatalysts the predominant *end-groups* were found to be terminal methylene groups, but in addition, evidence for the presence of tri-substituted ethylene groups was also found. The spectra of 2, 4, 4—trimethyl pentenes—1 and —2 were used for reference. (3) In none of the spectra was there any trace of —OH bands in the 3000 cm^{-1} region. In the spectra of polymers prepared with CCl_3COOH as cocatalyst there was evidence for the presence of methyl and possibly also ethyl trichloracetate. The spectra of methyl, ethyl, and t-butyl trichloracetates were recorded and used for reference. The presence of methyl and (possibly) ethyl esters is provisionally ascribed to the action on the reaction products of the methylated spirit which was added to the reaction mixture to inactivate and precipitate the catalyst. The question whether the polymer contains any trichloracetate end-groups remains open, and is being investigated further.

With reference to the preceding paper in this symposium, by Dainton and Sutherland, we also have found a band at 1105 cm^{-1} in the spectrum of low M.Wt. polyisobutenes produced with H_2O, CCl_3COOH and H_2SO_4 as cocatalysts to $TiCl_4$. We have been unable to identify this band, and think it is unlikely to be due to a tertiary alcohol group as suggested by Dainton and Sutherland, as there is no evidence in our spectra in the 3000 cm^{-1} region for the presence of —OH groups.

References.

(1) Thompson and Torkington, Trans. Farad. Soc. **41**. 246. (1945).
(2) Dainton and Sutherland, J. Polymer Sci. **4**. 37. (1949).
(3) A.P.I. Res. Proj. 44. Nat. Bur. Stand. Washington
Infra-red Spectrograms Nos. 276, 277.

4.—*FRIEDEL-CRAFTS COMPLEXES.*

Kinetic Examination of the Reactions of Di-isobutene Catalysed by Boron-Trifluoride Complexes

By

Alwyn G. Evans and F. T. Perkins,
Manchester University.

We have followed dilatometrically the homogeneous isothermal reactions of di-isobutene catalysed by a boron-trifluoride-cocatalyst complex. The cocatalyst used was a phenolic compound, and for any experiment the compound used as cocatalyst was also used as the solvent.

Class (*a*) reactions, in which p-chlorphenol, thymol, 3.5.xylen-l-ol and carvacrol were used, consisted in the dimerisation of the di-isobutene, and the rate was found to be second order in di-isobutene.

Class (*b*) reactions, in which phenol, o-cresol, m-cresol, and p-cresol, were used gave a reaction mixture which yielded a solid product when it was treated with caustic potash at the end of the reaction. For the case of m-cresol, this product was shown to be the ether, and this etherification reaction was first order in di-isobutene. For p-cresol, o-cresol and phenol the agreement with a first order relation fell off markedly along this series.

The etherification rate for m-cresol was second order in catalyst. For the dimerisation reaction using thymol, the order in catalyst was not so clearly defined, but the closest agreement was for second order. The plot of log k against $\frac{1}{T}$ gave slopes of $-\frac{9{,}900}{2.303\,R}$ and $-\frac{18{,}900}{2.303\,R}$ for the case of m-cresol and thymol respectively.

For all these reactions one mole of catalyst produced many moles of product.

It was found that when bubbling BF_3 into the phenol, ROH, to make the catalyst, the BF_3 was very soluble up to an amount corresponding to a molar ratio of $BF_3.2ROH$. This suggests that the catalyst is present as the ions $F_3\overset{-}{B}O\underset{R}{}\ \overset{+}{H}O\underset{R}{H}$.

It was thought that the second order in catalyst could possibly be explained if the effective catalyst were the 1:1 complex $F_3BO\underset{R}{H}$, and its concentration were governed by the equilibrium :—

$$F_3BO\underset{R}{H} + HO\underset{R}{} \overset{K}{\rightleftharpoons} F_3\overset{-}{B}O\underset{R}{} + \overset{+}{H}O\underset{R}{H}$$

in which the equilibrium lay well over to the right and in which the ionic complex $F_3\overset{-}{B}O\underset{R}{}\ \overset{+}{H}O\underset{R}{H}$ were completely dissociated. Then $[F_3BO\underset{R}{H}]$ would equal

$\frac{K.[catalyst]^2.}{[ROH]}$ The question as to whether this ionic complex is completely dissociated or not, has been tested by conductivity measurements. (A. G. Evans and S. D. Hamann). It was found that the conductivity of such solutions was far lower than would be expected if dissociation of the complex $F_3B\bar{O}\overset{R}{}\ .\ \overset{+}{H}O\overset{R}{}H$ were complete.

If all the BF_3 in solution were present as the undissociated ionic compound $F_3B\bar{O}\overset{R}{}\ .\overset{+}{H}O\overset{R}{}H$, the right order of reaction for the dimerisation would be given if, in one step, a proton transfer took place from the cation of one ion pair through two di-isobutene molecules (which are thereby linked together) to the anion of second ion pair. This mechanism would be very cumbersome, however, and very different from the mechanism associated with a polymerisation reaction (to which this dimerisation reaction is closely related).

We, therefore, do not wish to postulate any mechanism for these reactions until further work is carried out.

Friedel-Crafts Complexes and the Initiation of Polymerisation

By

M. H. Dilke and D. D. Eley[1],
Bristol University.

In initiating polymerisation, Friedel-Crafts catalysts must accept electrons, either from the monomer or from a cocatalyst molecule. We should therefore expect a relation between their electrophilic tendency and their activity as catalysts.

Calorimetric measurements of the heat of complex formation with benzaldehyde have been made, and used to deduce the halide-benzaldehyde bond strength. This is found to vary from about 54 *k.cal*/mole for aluminium iodide to about 4 k.cal/mole for antimony trichloride, in the order $AlI_3 \rangle AlBr_3 \rangle AlCl_3 \rangle FeCl_3 \rangle SbCl_5 \rangle TiCl_4 \rangle SnCl_4 \rangle (BF_3) \rangle ZrCl_4 \rangle SbCl_3$. There is some doubt about the position of BF_3, since in this case the heat of complex formation was not measured directly, but estimated by a displacement method. Possible weak complexes may be formed with $BeCl_2$, $ZnCl_2$, $FeCl_2$, and Cu_2Cl_2, but none with AlF_3, $CaCl_2$, $HgCl_2$, $SnCl_2$, $CuCl_2$, or hydrated ferric or stannic chlorides.

The relative order of activity in Friedel-Crafts reactions is quoted in the literature for several different reactions (*e.g.* acetylations, Gatterman-Koch reaction, racemisation of *a*-phenyl ethyl chloride, polymerisation of isobutene). With minor displacements, which may be due to differences in solubility or lack of quantitative data on true velocity coefficients, this order of activity in general follows the above order of bond strengths. The catalysts most frequently used in polymerisation, however ($SbCl_5$, $TiCl_4$, $SnCl_4$, BF_3.) lie in the middle of the table of bond strengths.

[1] More detail of this work may be found in J. Chem. Soc. 1949. 2601.

Discussion.

A. G. Evans: The approximate degree of dissociation of the $F_3BO^-.HOH^+$ (R R) compounds has been determined from conductivity measurements, by calculating the equivalent conductivity on the assumption that all the BF_3 in solution is present as the ionic compound, and dividing this value by Λ_∞ obtained by Walden for quaternary ammonium picrates in phenol (Z. Ph. Ch., *A*.**162**. 1. (1932)). This ratio was found to be about 1/1000. In solutions containing hydrocarbon in comparable concentration to that obtaining in an actual kinetic experiment the conductivity was extremely small.

D. D. Eley: A negative test of conductivity cannot be said, with certainty, to rule out the existence of ions in organic solvents, where the ordinary picture as found in aqueous solutions is complicated by the formation of ion-clusters (Eck, Ann. Physique, **4**. 12. 1949). The ionisation of carbonium ions is not simply determined by the dielectric constant of the solvent, but takes place only in specific ionising solvents.

M. G. Evans: The absorption spectrum of carbonium ions should show a shift towards the visible according as the ions are more strongly associated with the solvent. Is there any evidence that this shift depends on the dielectric constant of the solvent?

S. D. Hamann: In solutions which show high conductivity, for example, Ph_3CCl in SO_2, the absorption peak at about 435μ is sharp. In solutions which show low conductivity, *e.g.* Ph_3CCl in m-cresol, the absorption at this wavelength is broader. The effect of ion association on the absorption spectrum may thus be to broaden the absorption band. We have found this broadening of the band for the ion $Ph_2CCH_3^+$ in cases where the dielectric constant of the solvent is low.

E. T. Perkins: In reply to Mr. C. M. van Battum's question concerning the possibility of alkylation of the m-cresol by the di-isobutene, Emile Levas (Ann. de Chim. **3**. 170. (1948)) has studied the reactions of cyclohexene and phenols in presence of boron trifluoride, and has found that the formation of an ether, an alkylated phenol, or an alkylated ether, are all possible, and may all occur either singly or mixed as end products of the reaction depending on the experimental conditions used. The formation of an ether, however, is favoured by room temperature and low catalyst concentration. Such conditions were used when studying the reactions under isothermal conditions reported in this paper; the temperature was 28°C., and the catalyst concentrations about 0.3% molar BF_3 in phenol or cresol. Furthermore, analysis of the reaction mixture after reaction between m-cresol and di-isobutene had taken place showed the presence of a single product, which was identified as the ether.

P. H. Plesch: Some of the facts concerning the activity of catalysts and cocatalysts in the polymerisation of isobutene are summarised in the following table. Plus and minus signs indicate presence or absence of cocatalytic activity; the figures in brackets refer to the references at the end.

	Low Temp. (about—80°C.)			Room Temp. (0°C.—20°C.)	
	$SnCl_4$	$TiCl_4$	BF_3	$TiCl_4$	BF_3
H_2O	+ (1)	+ (2)	+ (4)	+ (5)	+ (7)
t-butanol ...	— (1)	— (3)			+ (8)
CH_3COOH ...		— (3)		— (6)	+ (9)
$CH_2ClCOOH$ ...		— (3)			
$CHCl_2COOH$ ...		? (3)		+ (5)	
CCl_3COOH ...		+ (3)		+ (5)	

If the polymerisation of isobutene is initiated by a proton, the initiating power of a catalyst-cocatalyst complex will depend on its acid strength with respect to the monomer as base. The acidity of the complexes is a composite quantity, being made up of the inherent acidity of the cocatalyst and enhancement by the catalyst. This is due to the electron withdrawal from the O—H bond of the cocatalyst by the co-ordination of the hydroxyl oxygen or of an adjacent carbonyl oxygen on to the catalytic halide. Considering acetic acid at room temperature, the electron withdrawal from the O—H bond due to $TiCl_4$ is insufficient, that due to BF_3 sufficient to loosen the O—H bond to the required degree. Considering $TiCl_4$ at low temperature, the inherent acidities of acetic and monochloracetic acids on the one hand, and of trichloracetic on the other, are respectively insufficient and sufficient to give the requisite resultant acidity to the respective complexes. In the case of dichloracetic acid and $TiCl_4$ the change of temperature from —75°C. to 0°C. increases the composite acidity of the complex, so that the cocatalytic activity, which is very slight at —75°C., becomes strong at 0°C. The activity of water as cocatalyst compared with the inactivity of t-butanol can probably be explained in terms of its greater inherent activity. The inactivity of acetic acid compared with the activity of water may be due to the fact that with the acid the carbonyl oxygen is co-ordinated to the halide, so that the electron-withdrawing effect of the halide is distributed to the two single bonds of the carbonyl carbon atom, and the resultant effect on the distant O—H bond is inadequate.

These preliminary considerations leave out of account possible solvation effects of polar solvents and possible resonance stabilisation of the composite anions.

References.

(1) Norrish and Russell, Nature, **160**. 543. (1947).
(2) Plesch, Polanyi and Skinner, J.C.S. 1947, 257.
(3) Plesch, Nature, **160**. 868. (1947).
(4) Evans (A.G.) and Meadows, in the press.
(5) Flett and Plesch, in the press.
(6) Plesch, unpublished.
(7) Evans, Meadows and Polanyi, Nature, **158**. 94. (1946).
(8) Evans and Polanyi, J.C.S. 1947. 252.
(9) Evans, Meadows and Polanyi, Nature, **160**. 869. (1947).

5.—*THE EFFECT OF TEMPERATURE.*

Some Observations on the Effects of Temperature on Ionic Polymerisations.

By

F. S. Dainton,
Cambridge University.

1.—*General.*

The following generalisations appear to hold in reaction kinetics. Exothermic reactions involve creation of new or stronger bonds, and when they are also association reactions involving minimum mass displacements within the reacting units, will possess only very low energies of activation. Considerable entropy is lost in these reactions, and the frequency factor will therefore be lower than the collision theory value. The propagation reaction and mutual termination by combination are processes which fall into this category. The reverse of the propagation reaction (referred to subsequently as the depropagation reaction) will have a large energy of activation (exceeding that of the propagation by an amount equal to the heat of polymerisation) and a positive entropy of activation. All other polymerisation processes, which include transfer, dismutation, mutual termination, and catalyst regeneration termination, are displacement or exchange reactions, and will have minor entropy changes but appreciable energies of activation.

The purpose of the present paper is to consider (*a*) the cause of the low energies of activation in ionic polymerisations, and (*b*) the competition which may arise between propagation, transfer and depropagation reactions as the temperature is raised, and the effects of such competition on the rate and molecular weight.

2.—*Energies of Activation.*

In spite of the scarcity* of systematic measurements of the temperature dependence of the rate of monomer consumption (**R**) and average degree of polymerisation ($\bar{\mathbf{P}}$) there is little doubt that E_i and E_p in ionic polymerisations are much less than the corresponding values for radical polymerisations. These differences may arise as follows:—

The energy necessary to uncouple the π electrons of the C=C double bond is $\sim$ 24 k.cal./mole (1). The measured values of E_p in radical polymerisations are less than this because a substantial part of the energy of formation of two C—C single linkages in place of a C=C double linkage becomes available in forming the activated complex. Now the maximum amount of such energy which could be so used is the heat change in the reaction

$$R^\circ + \begin{array}{|c|c|}\hline | & | \\ C=C \\ | & | \\ \hline \end{array} \longrightarrow \begin{array}{|c|c|}\hline | & | \\ R—C—C^\circ \\ | & | \\ \hline \end{array} \quad (R^\circ = \text{radical})$$

and must have the same value as in the reaction

$$R^+ + \begin{array}{|c|c|}\hline | & | \\ C=C \\ | & | \\ \hline \end{array} \longrightarrow \begin{array}{|c|c|}\hline | & | \\ R—C—C^+ \\ | & | \\ \hline \end{array} \quad (R^+ = \text{carbonium ion})$$

namely the overall heat of polymerisation (q), which is independent of the reaction mechanism. Hence if E_p (ionic) is less than E_p (radical) either (*a*) a larger fraction of the energy q becomes available to the activated complex in the ionic case than in the radical case or (*b*), an additional source of energy exists in the ionic reaction. Since there is reason to believe that E_p (ionic) is actually sometimes less than 24-q (*b*) is the correct explanation. Such a further source of energy could be the electrostatic energy between the ion and the dipole induced in the ethylenic link. The magnitude of this energy is $\alpha e^2/2\varepsilon r^4$, where α is the polarisability of the ethylenic linkage, e the charge on the ion, ε the dielectric constant and r the distance of the ion from the centre of the C—C link. Taking $\alpha = 4 \times 10^{-24}$ cc., $\varepsilon = 1$, the value of the attraction energy of the carbonium ion for a monomer 3Å distant is $\sim$8 k.cal./mole. It would therefore not be in any way surprising if E_p approached zero in ionic polymerisations.

There are two important corollaries to the conclusion that E_p is zero. First, since E_t and E_{tr} (termination and transfer respectively) are probably appreciable (*v. supra*), $\bar{\mathbf{P}} = k_p(m_1)/\Sigma$ (termination + transfer) will decrease with temperature, even at low temperatures where depropagation can be neglected. This is commonly observed (2). Secondly, the addition of the cation formed from the catalyst to a monomer to form the first carbonium ion is the true initiation process, and will be very similar in reaction path to the propagation reaction. Therefore, in all probability, the true value of E_i is zero. The observed value is finite, and this will be the energy necessary to achieve the initial charge separation, *e.g.* will be ΔE for the reaction $2I_2 \rightleftharpoons I_3^- + I^+$ in iodine catalysed polymerisations. The value of ΔE, and hence the apparent value of E_i, will be less the greater the dielectric constant of the solvent, as has been observed (2).†

* But see other contributions to this discussion.

† Discussed in more detail in the discussion.

3.1. *Competition between Propagation, Depropagation and Monomer Transfer.*

Reasons have been given for the following relations between the only types of reaction involving monomer molecules and growing chains in ionic polymerisations.

Propagation	Transfer	Depropagation
$m_1 + m_j^+ \longrightarrow m_{j+1}^+$	$m_1 + m_j^+ \longrightarrow m_j + m_1^+$	$m_j^+ \longrightarrow m_1 + m_{j-1}^+$
ΔS_p negative	$\Delta S_{tr} \approx 0$	$\Delta S_d = -\Delta S_p$ i.e. positive
E_p probably zero	E_{tr} considerable	$E_d = E_p - q$.

and therefore as the temperature is raised transfer and depropagation compete more and more effectively with propagation. This competition, combined with the influence of temperature on the remaining processes, determines the variation of $\mathbf{R}$ and $\bar{\mathbf{P}}$ with temperature.

3.2. $\mathbf{R}$ *as a Function of Temperature—Ceiling Temperatures.*

The temperature dependence of the rate of any polymerisation reaction proceeding by the chain mechanism is given by

$$\mathbf{R} = \Sigma(m_j^*) \cdot \{A_p \cdot (m_1) \cdot e^{-E_p/RT} - A_d \cdot e^{-(E_p - \Delta H)/RT}\}$$

Where A and E have their usual significance, and $\Sigma(m_j^*)$ is a function of the initiation and termination reactions only, and usually increases steeply (but in photochemical reactions may decrease slightly) with temperature. In either event, $\Sigma(m_j^*)$ cannot be zero, and any departures of the observed log $\mathbf{R}$—$1/T$ plot from the Arrhenius Law in a negative sense must be due to appreciable depropagation. The extensive implications of this have been discussed elsewhere (3), but for the present we are concerned with the fact that whatever the form of $\Sigma(m_j^*)$ the reaction rate of all polymerisation reactions must fall to zero at a temperature T_c, called the "ceiling temperature", such that

$$T_c = \frac{\Delta H}{R \ln A_p/A_d + R \ln (m_1)} = \frac{\Delta H}{\Delta S}$$

Here ΔH and ΔS are increments in H and S when 1 mole of monomer at standard molality (1 mole/litre) becomes 1/n th mole of polymer of $\bar{\mathbf{P}}$=n. Hence T_c is independent of the detailed mechanism of the reaction, and is in no way affected by the absolute values of A_p, E_p, $\Sigma(m_j^*)$. This has been clearly established in the case of polysulphone formation, which may take place through a free radical mechanism (benzoyl peroxide or light as initiating agents) or via an ionic mechanism (silver salts in liquid sulphur dioxide as catalysts).

These considerations are especially relevant to ionic polymerisations because carbonium ions are most readily formed when the carbon atom concerned is tertiary, the substituents being nucleophobic. Thus we are particularly concerned with

vinylidene type monomers which yield sterically strained polymers. In such cases ΔH is low(4) and we might expect T_c also to be low. Although rate-temperature data extending to the ceiling temperature are not available for any of the well known ionic polymerisations, all the evidence which does exist supports this conclusion. Thus work is in hand in this laboratory on α-methyl styrene which is known not to polymerise above 80°C., from which we conclude that $-\Delta H$ is probably not larger than 11 k.cal. I have recently been informed by Dr. R. Jessup of the National Bureau of Standards that his measurements of combustion heats of monomer and polymer substantiate this. It is likely that isobutene, for which $\Delta H = -12.7$ k.cal., also has a ceiling temperature only slightly above room temperature; and formaldehyde, which is polymerised to polyoxymethylene by formic acid in the vapour phase, must have a ceiling temperature in the vicinity of 130°C.

3.3. $\bar{\mathbf{P}}$ *as a Function of Temperature.*

The degree of polymerisation $\bar{\mathbf{P}}$ is the ratio of the net propagation velocity to the sum of the velocities of all processes leading to the formation of dead from growing polymer. Thus we obtain, for reactions with first order termination

$$\bar{\mathbf{P}} = \frac{A_p.e^{-E_p/RT} \cdot (m_1) - A_d.e^{-(E_p - \Delta H)/RT}}{k'_t + \Sigma k_{tr}[X]}$$

and for mutual termination

$$\bar{\mathbf{P}} = \frac{A_p.e^{-E_p/RT} \cdot (m_1) - A_d.e^{-(E_p - \Delta H/RT)}}{(I.k''_t)^{\frac{1}{2}} + \Sigma k_{tr}[X]}$$

where k'_t denotes the velocity constant of first order termination, and if this process involves any species other than the growing polymer (*e.g.* a retarder) the concentration of that species will be included in k'_t; k''_t is the mutual termination coefficient, I is the initiation rate and k_{tr} a coefficient for transfer with the agent X. These equations embrace all the possible types of behaviour, of which the most important are :—

1. *Low Temperature, Depropagation Negligible.*

(*a*) If $E_p > E'_t$ or $E''_t/2$ or E_{tr}, then $\bar{\mathbf{P}}$ increases with temperature. This has been observed in the photo-polymerisation of methyl methacrylate (6).

(*b*) If $E_p < E'_t$ or $E''_t/2$ or E_{tr} then $\bar{\mathbf{P}}$ decreases according to a law, $\log \bar{\mathbf{P}} = A/T + B$. This represents the usual behaviour in ionic polymerisations since E_p is so small.

(*c*) If $E_{tr} > E'_t$ or $E''_t/2$, and the frequency factors, etc., are such that over the temperature range concerned the dominant growth stopping agency changes from termination to transfer the $\log \bar{\mathbf{P}} - 1/T$ curve will be segmented, the slope changing from A to A', where $A' > A$. This is the state of affairs proposed by Eley and Richards(2) as being true in the $SnCl_4$ catalysed vinyl octyl ether polymerisation, although the data are not clear cut, and imply E_{tr} as large as 50 k.cal.

2. *Depropagation Appreciable.*

This will be apparent from the rate-temperature curve, and will lead to a $\bar{P}$—T curve which is concave to both axes, and a non-linear log $\bar{P}$—$1/T$ curve. A clear cut example is polysulphone formation (7), and it is possible that vinyl octyl ether also exemplifies this behaviour. In the vicinity of T_c the controlling factor in *all* reactions will be the marked depropagation. The experimental difficulty in detecting it is twofold ; (*a*) T_c may be high, and (*b*) transfer and termination may have already reduced $\bar{P}$ to small values.

4. *The Mobility of Ionic Polymerisation-Depolymerisation Equilibria, and the Analogy between this and Condensation-Evaporation.*

Unless the polymer is cyclic, or the growth stopping process has involved addition of a monovalent fragment of the catalyst, inhibition or transfer agent, it will contain a terminal olefinic linkage. This linkage should be capable of re-activation by any excess catalyst just as if it were the original monomer linkage. This is clearly shown by Eley and Richards observation that unless the catalyst (iodine) was promptly removed after 100% polymerisation of vinyl octyl ether, the polymer steadily increased in molecular weight. Strictly, the polymerisation could not have been 100% complete since some small amount ot monomer must always remain at the end of a polymerisation at any temperature.

Normally dead polymers are not readily depolymerised because of the difficulty of disrupting the molecule to form the active end, *i.e.* because E_i for the depolymerisation process exceeds E_i for the polymerisation. In ionic polymerisation we may expect these two activation energies to be nearly equal, for the reasons given in the preceding paragraph. Under these conditions chain centres may readily be regenerated from dead polymer molecules, and the equilibrium $m_1 \rightleftharpoons l/n.\ m_n$ may thus be rendered mobile, and the equilibriul state may be attained from either side in a reasonable time. In so far as the properties of a segment of monomer in the polymer are independent of the chain length n, this equilibrium will strongly resemble the phase change equilibrium between two states of aggregation.. The ceiling temperatures for gaseous monomer into liquid or solid polymer will thus be the analogues of boiling and sublimation points respectively. Appropriate analogies can be drawn for other conditions of polymerisation.

It will thus be observed that the ceiling temperature expression which applies to a gaseous monomer forming a solid polymer is, as this analogy suggests, really the Clausius-Clapeyron equation appropriate to sublimation. Measurement of dissociation pressures of polymers thus enables heats and entropies of polymerisation to be determined. The only example where these phenomena obtain is the equilibrium formaldehyde vapour $\rightleftharpoons$ solid polyoxymethylene, which is ionic and which has been discussed elsewhere (7).

REFERENCES.

(1) Hulbert, Harman et al. Ann. N.Y. Acad. Sci. **44**. 371. (1943).
(2) Pepper Trans. Faraday Soc. **45**. 397. (1949). Eley and Richards, Trans. Faraday Soc. **45**. 425. (1949).

(3) Dainton and Ivin, Nature **163**. 424. (1949). Dainton and Ivin, Trans. Faraday Soc. (in press).
(4) Evans and Tyrrell, J. Polymer Sci., **2**. 387. (1947).
(5) Carruthers and Norrish, Trans., Faraday Soc. **32**. 195. (1936).
(6) Melville and Mackay, Trans. Faraday Soc. **45**. 330. (1949).
(7) Dainton and Ivin, in course of publication.

Discussion.

P. H. Plesch: The following phenomenon may possibly find its explanation in terms of the considerations presented by Dainton. If isobutene is passed through a plug of activated clay in a glass tube, low molecular weight polymer is formed rapidly, and the clay is thoroughly wet with this fairly high boiling liquid (Lebeder and Filonenko, Ber. 1923). When the flow of isobutene is stopped, the clay dries completely in a few seconds. It is unlikely that this is explicable by evaporation : it may be a case of depolymerisation.

G. W. Meadows: If a mixture of isobutene and boron trifluoride is condensed together in the presence of a trace of cocatalyst, and then allowed to warm up to room temperature, a solid high molecular weight polymer is formed. If this is allowed to stand at room temperature without removing any of the components, the opaque white solid becomes transparent and gradually changes to a viscous liquid. This indicates that depolymerisation is taking place. If, however, we first remove the catalyst, either by prolonged pumping or by addition of excess alcohol or ether, the high molecular weight polymer is then obtained in a form which is stable at room temperature.

D. D. Eley: Dr. Dainton's suggestion that depropagation rather than transfer is responsible for the rapid diminution of molecular weight at high temperatures is a valuable one which we shall bear in mind in extending our work on vinyl octyl ether. Up to 50 or 60°C. measurements of the rate show no evidence for a ceiling temperature in the polymerization catalysed by stannic chloride or iodine. We are inclined to conclude that transfer is the dominant factor in the fall off of molecular weight over 50—60°C. To detect the onset of depropagation we need to extend the accuracy and temperature range of our experiments, which we shall hope to do. From Dainton's theory, since $\Delta H \sim 14{,}000$ cal., and our monomer concentration is about 0.6 mole/litre, we should expect a ceiling temperature of 193°C., which is considerably above the highest temperatures in our experiments to date.

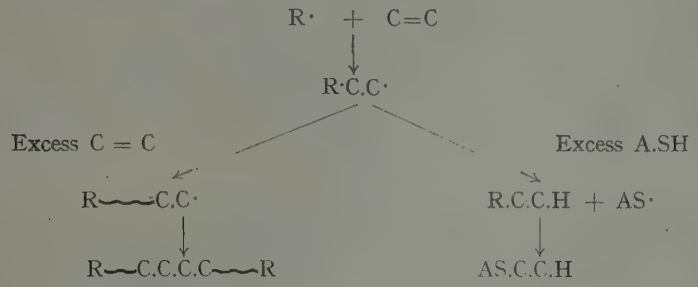
R. F. Tuckett: My observations concern general theory rather than the specific points discussed so far. In studying radical polymerisations, the work of the last few years has revealed the very close connection between the processes of polymerisation and chain transfer on the one hand, and those of addition to double bonds on the other ; in particular, the work of Kharasch and his co-workers has been especially illuminating. Arising from the discussions of the past few days, an analogous synthesis should now be possible for ionic polymerisations.

If one considers the addition of a molecule such as HBr to a double bond compound (C=C), this can occur in two ways, either through a radical chain process

or by a non-chain ionic one. Let us take the radical mechanism first. This is catalysed by peroxide traces, and the most likely mechanism is a radical chain of the type

$$\begin{aligned} R\cdot + C{=}C &\longrightarrow R.C.C\cdot \\ R.C.C\cdot + HBr &\longrightarrow R.C.C.H + Br\cdot \\ Br\cdot + C{=}C &\longrightarrow Br.C.C\cdot \\ Br.C.C\cdot + HBr &\longrightarrow Br.C.C.H + Br\cdot \end{aligned}$$

A similar mechanism can be written down for mercaptan addition (Waters, Chemistry of Free Radicals, p. 189). Now this scheme is very similar to that which produces polymerisation and if monomer is the predominating component in the system, then polymerisation occurs instead of addition across the double bond; in fact the two schemes can be combined into a single one, as shown below, for mercaptan. A.SH as the adding molecule



Intermediate cases also fit into this scheme, namely, the production of modified polymer containing mercaptan end-groups by the reaction of

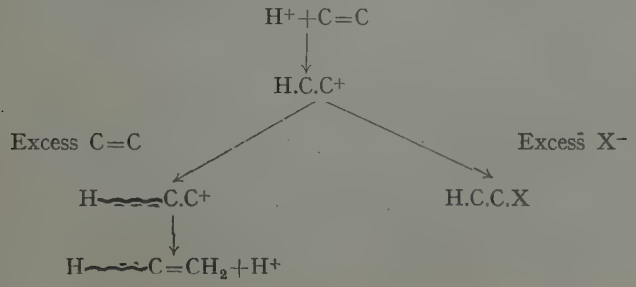
$$\begin{aligned} R{\sim\!\sim}C.C\cdot + A.SH &\longrightarrow R{\sim\!\sim}C.C.H + AS\cdot \\ AS\cdot + C{=}C &\longrightarrow AS.C.C\cdot \end{aligned}$$

The formation of compounds of the type $AS.(C.C)_2H$, as discovered by Kharasch, is another example of this mixture of two reactions at the other end of the scale.

In the absence of radicals, addition to double bonds takes place by an ionic mechanism, according to the Marlownikoff rule

$$\begin{aligned} H^+ + C{=}C &\longrightarrow H.C{=}C^+ \\ H.C{=}C^+ + Br^- &\longrightarrow H.C.C.Br \end{aligned}$$

(In the radical addition of HBr, this rule is reversed and the two mechanisms can be distinguished). This is not a chain reaction and so a similar scheme covering both ionic addition and polymerisation can be written down



The final stage of conversion of 'live' into 'dead' polymer may require the presence of a negative ion (X^-) in the immediate vicinity, but the important point is that, if a proton expulsion occurs in the termination mechanism, as Dainton's work shows quite convincingly, then it is equally possible as a reversible stage in the initiation process, which should accordingly be written

$$H^+ + C{=}C \rightleftharpoons H.C.C^+$$

The existence of substitution reactions and the isomeration of olefines by protonic catalysts supports this idea, and it should be very possible to pick it up by the use of deuterium ion (D^+).

This scheme does not include any mechanism involving monomer transfer, as put forward by Eley and Richards, and I rather doubt whether it exists; in radical polymerisations the case is different as the existence of monomer transfer arises quite naturally out of the mechanism of addition to double bonds. In the radical case, all the steps in a polymerisation chain have now been shown to have their counterparts in small molecule chemistry; it seems at least reasonable that a similar correlation exists in ionic polymerisations; this may well be a guiding principle in deciding between rival mechanisms in this branch of polymeric chemistry.

SUMMARY.

The recent experiments described and discussed in this symposium have provided additional evidence of the ionic character of Friedel-Crafts polymerisations. Carbonium ions have been identified spectroscopically in mixtures of olefines and Friedel-Crafts catalysts, though not as yet in actual polymerising systems. Ionic processes are also revealed by the marked effect of the dielectric constant of the solvent. Polymerisations of this type have so far been carried out only in solvents of relatively low dielectric constant (in a few cases up to $\varepsilon=36$, but usually $\varepsilon\sim2$) where the concentration of free ions must be inappreciable owing to the large energy of charge separation. The ionic processes in these polymerisations must therefore involve ion-pairs rather than free ions, with the carbonium ion always in fairly close association with a *gegen* anion.

A simple and coherent mechanism has been proposed by Polanyi, A. G. Evans and co-workers for the polymerisation of isobutene by boron trifluoride hydrate and other catalyst-cocatalyst complexes. The initiation process is envisaged as the transfer of a proton from the complex to the monomer resulting in a tertiary butyl carbonium ion in close association with the anionic residue of the complex. The chain is propagated by successive additions of monomer to form larger carbonium ions which at every stage maintain this close association with the *gegen* anion. Termination is due to the loss of a proton from the polymer carbonium ion to the neighbouring anion, leaving a double bond in the "dead" polymer molecule, and regenerating the catalyst-cocatalyst complex. This theory of the polymerisation mechanism is confirmed by A. G. Evans and Meadows' demonstration that rigorously dried boron trifluoride will not initiate reaction. Infra-red absorption spectra of polyisobutenes observed by Dainton and Sutherland and by Flett and Plesch reveal the presence of an initial tertiary butyl group and a terminal double bond, as required by the theory. The proton transfer processes

in initiation and termination are demonstrated by Dainton and Sutherland's observation that when boron trifluoride deuterate is used as catalyst, deuterium appears in the polymer and the deuterate is progressively converted into hydrate.

Other polymerisations (vinyl ethers, styrene and the co-polymerisation of butene and sulphur dioxide by silver salts) are similar to that of isobutene, in that the polymer is unsaturated and many molecules of polymer are formed per molecule of catalyst, that is to say, a similar termination mechanism must operate. Kinetic studies of the polymerisation of vinyl ethers and of styrene indicate that the termination reaction is a first order process. This is in accordance with the isobutene mechanism if the polymer carbonium ion and its associated anion can be regarded as one kinetic unit, *i.e.* if they are in close association. The initiation process, however, must differ somewhat from that of isobutene, since no cocatalysts are necessary, at any rate with the catalysts used (iodine, stannic chloride, silver perchlorate and nitrate). Iodine and silver salts could give rise to simple cations which could play the part ascribed to the proton in the initiation of isobutene, but with stannic chloride it seems necessary to postulate some intermediate complex formation. In the $SnCl_4$-styrene polymerisation there is some uncertain evidence that cocatalysts are necessary in hydrocarbon solvents, but in ethylene dichloride and nitrobenzene they are not necessary, and it therefore seems likely that a catalyst-solvent complex may be formed which can provide the initiating carbonium ion. In vinyl ethers it seems possible that the monomer itself may act as cocatalyst; Hamann, Plesch and Skinner have given details of a possible mechanism.

A characteristic feature of Friedel-Crafts polymerisations is that the molecular weight decreases markedly with temperature, and that much lower molecular weights are obtained than in radical polymerisations at the same temperature. One reason for this could be the occurrence of chain transfer processes highly dependent on temperature. Such monomer transfer reactions have been postulated by Eley and Richards in the polymerisation of 2-ethyl hexyl vinyl ether. The extent to which transfer takes place depends on the catalyst, being considerable with iodine and silver perchlorate, but negligible with stannic chloride. So far, no other evidence has been offered of transfer processes in other Friedel-Crafts polymerisations.

Another explanation of the decrease of molecular weight with temperature is the reversal of the propagation reaction. Dainton and Ivin have shown that, as the temperature is raised, the depropagation reaction becomes more important until a temperature is reached (ceiling temperature) at which the net polymerisation rate and molecular weight become zero. Friedel-Crafts polymerisations are particularly susceptible to depropagation since the "dead" polymer contains a double bond and may, therefore, be easily reactivated. Relatively low ceiling temperatures are to be expected for some monomers susceptible to Friedel-Crafts polymerisation (*e.g.* *aa*'disubstituted olefines) because of their lower heats of polymerisation. The relative importance of transfer and depropagation reactions in limiting molecular weight has still to be investigated, but in principle their effects can be distinguished from the form of the molecular weight-temperature relation.

There are a number of special features shown by certain reactions which make it unwise to generalise too much at the present stage. For instance, the polymeris-

ation of isobutene by boron trifluoride or titanium tetrachloride appears to be a heterogeneous process, and may well differ in mechanism from the homogeneous polymerisations in solution. Initiation processes must differ in detail in different reactions according as cocatalysts are or are not, necessary. A further complication, only briefly mentioned in this discussion, is that in certain polymerisations (styrene with $SnCl_4$(1), with $SnBr_4$(2) and isobutene with $TiCl_4$(3)) a catalyst molecule or fragment may be incorporated in the polymer molecule. The extent to which this takes place appears to be variable ; in the styrene-$SnBr_4$ system recently studied by Landler(2) one in three polymer molecules formed under his conditions retains a catalyst molecule, but in many instances this fraction must be much smaller, since it is known that many polymer molecules can be formed per molecule of catalyst. At least two termination processes must therefore operate, one leading to catalyst incorporation, and one to an unsaturated polymer and regeneration of the catalyst. The relative importance of these two processes will presumably depend on the conditions of catalyst and monomer concentration, but quantitative information is lacking.

Despite these differences in detail, all Friedel-Crafts polymerisations so far studied have the same general characteristics, which now seem fairly well understood. All the effective catalysts are acids in the generalised sense of G. N. Lewis, that is to say, are strongly electrophilic. Their activity in initiating, however, seems due to outright transfer of a proton or other positive ion to the monomer rather than simple electron acceptance forming a co-ordinate bond. In some instances the catalyst itself may be capable of ionisation (*e.g.* H_2SO_4, $AgClO_4$,I_2) but in others, and especially with the Friedel-Crafts halides themselves, ionisation seems possible only through the intermediate formation of an ionic complex with added cocatalyst or with other polar substance. The monomer carbonium ion so formed, and the polymer ion during growth, are not to be thought of as free cations, but as part of an ion pair, *i.e.* as remaining in close association with the anion formed from the catalyst or complex residue. The termination reaction seems definitely to be a first order process, which is visualised as the spontaneous recombination of the polymer carbonium ion with its *gegen* anion, resulting either in incorporation of the catalyst or in expulsion of the whole complex (proton plus *gegen* anion) leaving a double bond in the polymer.

Much work remains to be done before these reactions are fully understood. In many systems qualitative information is still lacking as to the nature of the end groups and the presence or absence of catalyst fragments. The specific and general effects of polar solvents are still to be explored. Much more kinetic work is needed to identify and distinguish transfer and depropagation processes. The related field of anionic polymerisations is almost entirely unexplored.

References.

(1) Staudinger Die hochmolekularen organischen Verbindungen Berlin, 1932.
(2) Landler, Rec. Trav. Chim. **68**. 992. (1949).
(3) Plesch, Research, **2**. 272. (1949).